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White Discharges on Silk With Hydrosulphite

By **W. T. WHITMAN**

The production of white discharges with hydrosulphite on silk is perhaps one of the biggest problems that the print works colorist has to face, and consistent success along this line is only achieved by constant watchfulness and the ability to adapt conditions to meet any particular case. While the colorist, in order to conserve floor space in the color shop, and to avoid errors, will naturally strive to devise a formula for a white discharge that will work for all classes of goods that are being handled in the print room, yet it is greatly to his advantage, from the point of view of costs as well as results, to introduce modifications here and there in the formula to secure the best discharge possible in any particular case.

Suitability of Various Gums

EVERY man has his own preference as to gums, and indeed there is something to be said in favor of any particular gum—if no more than the fact that it is cheap. Gum arabic will give as good a white discharge as will any gum, but its use alone is expensive, especially when one takes into account the fact that there is inevitably a certain amount of waste when using this gum. The dry gum as received from the importers contains quite a large amount of sand which has been blown on to the partly dry gum as it oozed out of the tree, and this sand is locked up inside the lumps when the gum dries. When the gum is dissolved in water this sand is liberated, and in order to prevent it from getting into the discharge as prepared for the printing machine, it is necessary to allow the gum to settle at least overnight before using any of it, and even then the last five or ten gallons in the bottom of the barrel should not be used. Some of it can be saved by taking the bottoms from the barrels and mixing them together in another barrel, allowing them to settle again and using the gum off the top. But in any case there is always a certain proportion of the gum that must be thrown away, and the barrels must be well boiled out out before using again.

Neglect of these precautions means that one gets a printing gum containing a great deal of fine sand, some of which will pass through the straining rags even with repeated straining, and the printer will have infinite troubles with rollers being scratched and roughed and doctor blades being nicked.

Gum arabic is well known of course for its sharpness of mark and smoothness of print, and can be specially recommended, either alone or with the addition of Textile Gum, for the printing of fine lines, which are quite difficult to print. On weighted silks particularly there is a great tendency on the heavier loaded qualities for the lines to break and print in short sections instead of printing as a continuous line.

Gum Arabic is usually cooked at four pounds to the gallon. After the gum has been boiling for a while, it will foam up quite vigorously, and when this foaming has subsided the cooking is complete. Printing colors made with Gum Arabic look very much thinner than those made with other gums, but in spite of this they will be found to have the necessary good body for sharp printing.

Textile Gum is a prepared gum which is supplied ready for use by quite a number of manufacturers. It is the ideal gum for all-round work. Being grit free, it can be used right down to the last drop in the barrel. It has great thickening power, and will stand dilution with more than its own volume of water and still give a gum that is thick enough to print satisfactorily. It gives a good sharp mark and smooth, uniform prints, and it washes out quite readily after the aging or steaming, leaving the silk soft. The older brands were quite dark in color, and did not give so good a white discharge as Tragacanth or

Gum Arabic, but recently specially purified products have been put out on the market which are very clean and give splendid white discharges.

The biggest drawback to Textile Gum is the price, more especially in locations away from the centers of production, where transportation charges have to be taken into account. For this reason many colorists prefer to use a mixture of Textile Gum with some other thickener so as to cut down the costs.

From the point of view of the purity of the white discharge obtained, Gum Tragacanth, if a clean grade, is also very good. Like Gum Arabic, Tragacanth contains a lot of sand and must be settled out after cooking in the same way. Where Tragacanth is also used in the finishing room of the print plant it is a good idea to sift the dry gum through a sieve with a quarter of an inch mesh. In this way a great deal of the dirt is separated out, and the siftings can be used in the finishing room, while the cleaner portion is boiled up in the color shop for use in the print room. When cooked at eight ounces per gallon, Tragacanth gives a thickener that will stand about a two to one reduction with water. A little time in the cooking can be saved by swelling the gum in a barrel with cold water overnight, but in any case it takes 3 to 5 hours to cook Tragacanth smooth. This gum gives very good penetration—no small consideration in these days when converters are demanding that the back and the face of printed silks shall be indistinguishable. Its use is somewhat limited by its well known failure to give a sharp mark. It cannot be recommended for the printing of fine lines, but for the larger irregular objects it is sufficiently good. All practical men are familiar with the habit that it has, when water is added to it too quickly, of breaking up into lumps which are only smoothed out after long and vigorous stirring. However, the addition of a small amount of another gum will often obviate the necessity for this long stirring. Gum Arabic will smooth it out very readily, but the resultant mixture is too thin to be used, so that this is only resorted to when the discharge paste as prepared for the printing machine comes up too thick. Textile Gum, generally speaking, is very good for smoothing out Tragacanth pastes, although occasionally one will come across a brand of it that does not work so good. Most makes of Textile Gum do not thin the Tragacanth to any appreciable extent.

In the past few years a number of powdered gums have appeared on the market under such names as "Tragacanth Substitute," "Gum Gatto," etc., which are intended to replace Tragacanth for printing. They have a very definite price advantage over the original gum, being much cheaper per pound, and having about the same thickening power, weight for weight, as Tragacanth itself. A further advantage is that these substitutes are grit free, so that there is no wastage, and the cooked gum can be dipped out right to the bottom of the barrel without getting into trouble with scratches and streaks. Some of the earlier products had the disagreeable feature of going sour very quickly on keeping, but the later brands are a big improvement in this respect. It is always better, however, to add some formaldehyde or phenol to the gum after cooking in order to prevent the bacterial action which causes the souring. The substitute does not take so long to cook as does Tragacanth, which is another big advantage in shops where kettles are at a premium. Care must be taken in wetting out the gum, and some makers recommend alcohol for this purpose. A mixture of Pine Oil and water is also very good, although with good agitation in the kettles satisfactory results can be obtained using water alone. In order to prepare a batch of this gum, place a little water, with or without the other wetting out agents, in the bottom of the kettle, and add the powdered gum a little at a time with vigorous stirring. If the mixture gets too dry as more gum is put in, add water in a very thin stream until the gum wets out. When all the gum is added and has become thoroughly wet the kettle is filled up with water, better added slowly, and the steam turned on. One hour is usually sufficient to complete the cooking, except when Pine Oil has been used for wetting out, in which case the cooking takes a little longer. Tragacanth Substitute behaves just the same as Tragacanth itself in the printing machine, penetrating just as well but giving no sharper mark. The cooked paste is usually whiter in appearance than the average Tragacanth.

British Gum, which is widely used in printing, does not give a very good white discharge when used alone, but if it is mixed with Tragacanth the white is much improved. Such a mixture will give a mark sufficiently good for all but the most particular cases, and it washes out of the silk quite readily, while it is much cheaper than Textile Gum. A good combination is two parts of British Gum (4 pounds to the gallon) and one part of Tragacanth (8 ounces to the gallon). To make this, two-thirds of a kettle of British Gum is cooked in the regular way, and when the boiling is finished the Tragacanth, already cooked, is added and allowed to stir in while cooling.

This mixture of gums may be further mixed with Textile Gum to improve the mark and the smoothness of the print.

The Use of White Pigments in Discharge Pastes

Some years ago it was the custom to make up the discharge whites by merely mixing the chosen thickener with hydrosulphite solution and a little glycerine. More recently, and with the entrance of weighted silks into the field of prints, it has become common to supplement the hydrosulphite with some white pigment. This forms an opaque coating on the cloth and helps to cover the slight yellowish stain that is often left on the goods when the discharging action takes place. On weighted silks the white discharges obtained are always better if the printing paste is faintly alkaline, so that among the early attempts to get satisfactory whites the addition of a little soda ash to the paste was tried. Zinc oxide, too, is alkaline in nature, and also it clings to the cloth to some

extent, so that its use gives better results than the soda ash method.

The next step forward was the addition of egg albumen to the printing pastes. Under the action of the heat in the aging of the goods after printing this coagulates and holds the pigment on the cloth inside an insoluble envelope, so that it does not wash off and its presence gives the cloth a whiter appearance in the printed parts than it would have otherwise..

Zinc carbonate, lithopone, and Titanium oxide all have been used on a practical scale for improving the whiteness of the discharges. The last named is quite expensive, but it gives extremely good whites, and in practice it is usually applied along with some zinc oxide. The use of egg albumen in the discharges is apt to cause excessive foaming at the printing machine, which leads to defective printing unless corrected. Practical experience shows that it is better to add something to the discharge paste before sending it out to the printing machine in order to prevent this foaming, rather than wait for the paste to froth up and then try to kill the foam. Fusel oil is largely used in silk print shops to stop foaming of printing colors, but if used in excess in white discharges containing egg albumen it will coagulate the latter and cause the paste to work dry, so that the cleaning doctor will not function properly. There are other products on the market that act as foam killers and have no tendency to coagulate albumen. These are to be preferred to fusel oil.

On account of the large amount of insoluble matter contained in these pigment whites, they must be made with scrupulous care in the color shop. Any neglect will surely result in troubles at the printing machine, and consequent spoiled work. The pigment must be very carefully wet out and mixed so as to avoid lumpiness, and every successive step must be slowly and carefully carried out. A grinder is essential if good work is to be done, and the pasted pigment should be ground fine before being added to the thickener, as also must the finished white discharge before going out to the printing machine. The addition of Glycerine or Olive Oil will help the discharge to work smoothly in the printing machine, but an excess of these is to be avoided, as the printed objects would then fail to dry properly and there would be trouble with marking off on to the unprinted parts of the goods. The Egg Albumen is best added to the discharge just before it goes out to the printing machine. The usual practice is to prepare a solution containing 8 pounds of Egg Albumen per gallon. Half the required amount of cold water is placed in a pail and the Albumen crystals are sifted slowly on to the surface of the water. The rest of the water is then poured over the top of the layer of solid matter and the whole is left overnight, when solution will take place. This solution is added to the discharge as needed.

Tin weighted silks when printed with Hydrosulphite discharges always lose some of their strength in the printed parts, and this weakness is further aggravated by the coating of pigment and Albumen on the fibers, which makes them stiff and brittle, so that it is well to watch the strike-off patches on every pattern and see that the goods are not becoming unduly tender. If they are, it is necessary to reduce the amounts of pigment and albumen being used, even sometimes at the expense of the purity of the white discharge obtained. This is especially true when extremely heavily weighted goods are being handled.

A discharge containing 2 pounds of Hydrosulphite, 2 pounds of pigment, and 10 ounces of Egg Albumen (solid) per gallon is as strong as can safely be run on a printing machine, and in the case of large objects on cloths that have been excessively weighted these proportions will have to be cut down. Besides the tendering effect, pigment whites leave the printed parts harder than the rest of the goods, and this must be watched too in determining the amounts of pigment and albumen that may safely be used.

Running Troubles With White Discharges

White discharges, whether they contain pigments or not, are notoriously difficult to run in the printing machine. Troubles with nicked doctor blades and roughed rollers are usually due to the presence of grit or hard particles of pigment, and may be cured by further grinding or restraining. If troubles of this sort recur frequently it will often help to locate their origin if one can find out just what is the nature of the foreign matter that is causing the trouble. To do this, take about a gallon of the white discharge in a pail and add hot water with good stirring until the pail is full. Allow to settle for a few minutes and then decant carefully until only about a gallon of liquid is left in the bottom of the pail. Fill up with hot water again, settle and decant as before. Repeat this procedure until all the gum is gone and there is only clear water left in the pail. If there is any grit or hard foreign matter in the paste it will be found at the bottom of the pail and may be examined at leisure.

Another point to watch is that the albumen in the printing paste has not become coagulated. The coagulation by Fusel Oil has already been mentioned. Another source of trouble along this line is that sometimes the white discharge comes from the grinder quite hot, and if it has to be used before having a chance to cool down and the Egg Albumen solution is added, coagulation will occur and the paste will not work smoothly in the printing machine. The writer recalls an experience with a white discharge which persistently roughed the copper roller in the printing machine. Dilution with water in the manner suggested above showed that no particles of grit or hard lumps of pigment were present in it, so the cause had to be looked for elsewhere. It was noticed that the temperature of the discharge was quite a bit above the coagulating point of albumen, and so another pail of it was taken from the barrel and cooled down

before adding the albumen solution, and then sent out to the printing machine. After this had been done no further printing difficulties were encountered.

A more serious difficulty, however, is the annoying tendency of the white discharges to rip or tear the copper rollers during the printing. These rips or tears are serious because of the loss of production that results from the long time that is consumed in repairing them. Sometimes one has a printing paste seemingly free from grit and foreign matter, carefully and properly put together, which will run beautifully for a time and then suddenly, for no apparent reason whatever, it will rip the roller, raising up a ridge of copper that lifts the cleaning doctor, but strangely enough not roughing the edge of the doctor blade to any great extent. The most elaborate precautions in the preparing of the Hydrosulphite solutions used to make up the discharge, such as allowing to settle overnight and fine straining of the solution when adding it to the thickener, as well as a further fine straining of the discharge paste when ready for the printing machine, do not guarantee freedom from this trouble.

Opinion is divided as to the actual cause of this tearing of the rollers. Some hold to the theory that the churning of the paste in the color box, and the effect of the friction between the copper roller and the steel doctor blade, bring about a crystallization of the Hydrosulphite, in much the same way as solutions in the laboratory are often induced to yield crystals by rubbing the end of a glass rod against the side of the containing vessel. On the other hand it is contended by some that since an aqueous solution of Hydrosulphite at a strength of 4 pounds to the gallon is kept in the color shop for days at a time without crystallization taking place, and since it is very rare that the white discharge as supplied to the printing machine contains more than 2 pounds of Hydrosulphite per gallon, it is unreasonable to suppose that this paste with the weaker Hydrosulphite content could be induced to form crystals under any conditions.

It is further pointed out that if crystals are prepared by allowing a strong solution of Hydrosulphite to evaporate slowly at room temperature, it is not found possible to take one of these crystals between the fingers and scratch a copper roller with it. In fact if this is tried the crystal will often crush to powder under the pressure of the fingers as it is applied to the roller. Of course it must be admitted that this trial is made under conditions differing from those actually existing in the printing machine, and it is also quite possible that the fact that the copper roller has engraving on it will have some bearing on the question.

In a print room where these rips were of frequent occurrence, and where an alert printer occasionally managed to stop his machine before the rip had travelled all the way round the roller, careful observation showed that the beginning of the rip was almost invariably in some portion of the engraving. This suggests the idea that a crystal of Hydrosulphite may be carried up to the edge of the doctor blade in the engraving, and then be firmly held between the roller and the doctor, roughing the roller as it rotates against the blade. Under these conditions the pressure applied by the blade of the doctor against the roller is much greater than the force that could be exerted by hand. Another possibility that has been suggested is that the action may be due to the gouging out of a small piece of copper from the engraving, and this piece of copper, becoming jammed between the doctor blade and the roller, causes the rip. It is a fact that straining the discharge after it has ripped the roller will often show that particles of copper are present, but whether this is cause or effect is almost impossible to decide.

But whatever the theories on the subject, all are agreed that rips and tears do occur, with a serious loss of time and production in the print room. In order to try to avoid this trouble, some color shops make a practice of heating up the white discharge under a steam pipe and sending it out to the printing machine hot. This of course is only a partial remedy at the best, as the paste soon cools off in the color box, especially when printing a light pattern which removes the paste from the color box only very slowly. Further, a discharge paste containing Egg Albumen can not be heated up in this way, or troubles will ensue as explained in a previous paragraph.

The very best way, in the writer's opinion, of cutting down these rips and tears to an absolute minimum is to dissolve the Hydrosulphite not in water, but in a gum. The alternative of dissolving the Hydrosulphite in water, straining, and then using this solution instead of water in cooking the thickener, may also be used, but not in all cases, and experience proves that it is better to dissolve the Hydrosulphite in the gum. This method of dissolving direct in the gum has also the advantage of being much quicker. It might be thought that there is considerable risk in putting the solid Hydrosulphite direct into the gum, without previously removing the dirt by dissolving and straining, but in a practical way this difficulty does not seem to crop up. Of course one must be sure that a good grade of Hydrosulphite is being used, but that can soon be checked up by a solution and filtration test in the laboratory.

Objection might also be made to the idea of subjecting Hydrosulphite to the high temperatures necessary to dissolve it in the gum, but there does not seem to be any difficulty along this line. The one thing to watch out for is that no acid be allowed to get into the kettle by mistake. If this happens the Hydrosulphite will begin to decompose and the paste will froth violently and pour over the top of the kettle on to the floor. The decomposition will continue until all the Hydrosulphite is gone, and after the frothing has subsided a test will show that the thickener has no discharging power whatever. It is a waste of material to try to use up this thickener by adding more Hydrosulphite, for the decomposition will only recommence as soon as fresh material is added.

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A Method for Distinguishing Between Old and New Cotton Fibers*

By A. W. WINNE and J. DAVIS DONOVAN

Many of the American states have passed laws requiring the kind and nature of materials used in filling bedding and upholstered furniture to be disclosed to the purchaser, usually by means of a statement on a cloth tag attached to each article. Most of these laws require that material which has had previous use be labelled secondhand, and one of the most difficult problems for those charged with the enforcement of the laws has been the detection of secondhand cotton filling that has been described as new material. No visible change appears in cotton fibers as a result of previous use and laboratory tests have been unsatisfactory and inconclusive.

THE Maryland State Health Department is charged with the enforcement of the state laws relating to bedding and upholstered furniture. The fact that various textile fibers present characteristic fluorescences in ultraviolet light enabling them to be differentiated from each other, is a matter of recent knowledge. The Department has carried on a number of experiments to determine whether or not the fluorescent method could be used to differentiate between old and new cotton fibers, as well as to distinguish cotton from other textile fibers.

Ultra-Violet Radiations

Fluorescence is the power of a substance to absorb certain wave-lengths of light and to re-emit the energy in longer wave-lengths, as light, instead of turning it into heat. A substance exhibiting fluorescence will do so only under the effect of the incident radiations; when they are removed, no fluorescence is observed. Only substances which have absorption lines in the region of 4,000 to 3,000 Angstrom units show visible fluorescence. Cotton generally gives a violet fluorescence when observed under radiations of light in the ultraviolet region of the spectrum.

In our experiments, a mercury quartz arc lamp was used as the source of the ultraviolet radiations and a Corning glass filter of 3 mm. thickness was found to be the most suitable sort for this work. A filter which allows the passage of rays from about 4,047 to 2,900 Angstrom units gave the best results.

Changes with Grade of Fiber

As the range of the visible spectrum extends from about 7,000 to 3,900 Angstrom units, it will be noted that this filter allows a very small amount of the visible violet light to pass through.

When various samples of new cotton fibers are examined under the ultraviolet light, with such a filter, one immediately notices that the degree of intensity of the violet fluorescence changes with the grade of fiber. This degree of intensity varies from a pale violet in long-staple fibers to a deep violet in a low-grade linter; that is, the nearer the seed hull is approached, the deeper the violet fluorescence. The fluorescence of cotton depends on the nature of the fiber, the kind of cellulose (usually negligible in this work) and the natural color of the cotton. By using a Wood's filter all of the visible radiations were filtered out and the fluorescence of the cotton fibers was so materially reduced that this method of differentiating between samples of cotton proved of little value.

Influence of Age

As cotton ages, the fluorescence turns from a violet to an ivory-white or brownish-white color, with the probable change of cellulose to oxycellulose. Pure cellulose produces a violet fluorescence, while oxycellulose, on the other hand, gives a strong ivory-white color. When corresponding samples of new and old cotton fibers were examined, a distinct change in their fluorescence was noted. When fibers were taken from the center of bales of a known age and examined under the ultraviolet radiations, it was found that they had a fluorescence similar to that of new fibers, and those from the outside of the bale showed a very slightly lighter fluorescence. One bale used in the experiment was two years old and another had been in a government warehouse for more than five years. These findings, with others, which will be described later, gave support to the theory that the cotton cellulose changes to oxycellulose with exposure to light, moisture or air with an accompanying change in its fluorescence in ultraviolet radiations.

Fluorescence of Hydrocarbons

Investigators have found that unsaturated hydrocarbons are non-fluorescent, while saturated hydrocarbons exhibit a strong bluish fluorescence. Cotton fibers are covered with a very thin oil and wax film. This film is composed of saturated hydrocarbons and fatty acids and extremely minute quantities of some unknown substances which have not been identified. This oil and wax film makes up about five-tenths of one per cent of the cotton by weight. Since the greater part of this weight is fatty acids which show a bluish fluorescence under ultraviolet light we should expect to find a diminution of the intensity of the actual violet fluorescence of the cotton cellulose. In our examinations, when we treated the sample with some suitable solvent to remove the oil and wax film, a deeper violet fluorescence was observed than in the sample orig-

*From the Laboratories of the Maryland State Department of Health, Baltimore, Maryland.

inally. These reactions seem to indicate that the fluorescence observed in the ageing of cotton is not because of film on the surface of the cotton fibers but is the direct result of an oxidation of the cellulose structure of the cotton fiber itself. Evidence favoring this conclusion may be had from the fact that when the film has been removed from the fibers of a sample of cotton, oxidation proceeds much more rapidly than in a corresponding untreated sample. It is apparent that this film also acts as a protective film and prevents earlier deterioration of cotton than would occur without the oil and wax coating.

Flesh-Colored Appearance

A number of examples which exhibited spots of yellow or flesh-colored fluorescence under ultraviolet radiations were among those examined. This usually occurred with the kind of cotton giving the violet color, in small spots at random in the sample. No particular change was noted after subsequent treatment with various solvents. Other investigators have observed this flesh-colored fluorescence in cotton. The nature of this cotton was not investigated since it was encountered only in small areas and usually in samples of new cotton.

While the extracted oil and wax seemed to have a somewhat pale bluish fluorescence of its own in solution, it is apparent that this could not be the underlying cause of the fluorescence color change. The solvents used in making extractions included alcohol, ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, etc. Carbon disulphide seemed the solvent best suited for this extraction, as it has no fluorescence under ultraviolet radiations, while the others show some fluorescence. Acetone was unsuitable because of a pronounced bluish fluorescence noted. When examination of liquids was necessary, a quartz test vial was used to hold the liquid materials for exposure under the light. Quartz was used because it is non-fluorescent in ultraviolet light, while glass does fluoresce slightly—enough to mask the fluorescence in some cases if it be very faint. It was also found that the fluorescent colors containing the liquids was viewed against a dark background.

Deepening of Flouescence

Our examination showed that treatment of cotton fibers with various solvents deepens the violet fluorescence, at least temporarily. However, if a sample of cotton were merely wetted with the solvent and allowed to dry, it returned to its former fluorescence color. If, on the other hand, a sample were washed with the solvent several times and then allowed to dry, it would not immediately return to its former color, but remained a deep violet. Subsequent experimental work showed that this last sample lost its deep violet color much more rapidly than if untreated, and it approached the usual ivory-white fluorescence characteristic of known secondhand or old bedding materials. This result agrees with the conclusion previously referred to regarding acceleration of the oxidation of cotton cellulose when the oil and wax film had been removed.

We found, however, that if machine oil, either from a manufacturing process or from some other cause was present on a sample of bedding material, the natural fluorescence of the sample was masked and a true determination of its history was difficult if the fluorescence test alone were used. If the sample was treated with a solvent, both the machine oil and the natural oils and waxes were removed with the consequence that a violet fluorescence was observed. This was not so marked in old material as in new.

Exposure to Atmosphere

Samples of new bedding material when merely boiled several times with distilled water and allowed to dry also assumed a deeper violet color than originally. These samples, too, lost their deep color very much more readily than the untreated samples of the same materials.

Another interesting experiment, in agreement with results discussed heretofore, consisted of exposing two samples of the same material to outdoor conditions. One sample was kept dry. The other sample was wet with water thoroughly every day. The samples were mounted beside each other and exposed to the direct rays of the summer sun for three months, averaging about eight hours exposure a day. Examination under the ultraviolet lamp showed that the dry sample gradually lost its fluorescence and at the end of three months' period had changed from the violet color characteristic of new cotton, well toward the ivory-white color observed in the case of old cotton. The sample which was wet daily, became a deep violet color at first, deeper than originally; this gradually changed to a lighter violet and after three months appears to be slowly changing to a pale violet, which ultimately will probably become ivory-white. It is believed that much of the oxycellulose, as fast as formed, was removed immediately by the water washing and therefore was unable to accumulate sufficiently to show any appreciable change in fluorescent color except after a long time. Progress of the exposure was noted every few days under the ultraviolet lamp.

Congo Red Test

The microscopical examination of damaged cotton fibers by the Congo Red test of Bright was tried on various new and old samples of cotton fibers. Cotton fibers attacked by fungi, exposure to heat, mechanical damage, etc., are sensitive to this test. These are conditions to which secondhand bedding materials may have been exposed. The test depends on the swelling of the cotton fibers with an 11 per cent sodium hydroxide solution and staining with Congo Red dye. Where the outer cuticle of the cotton fiber is damaged by one or more of

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Proceedings of the American Association of Textile Chemists and Colorists

The American Association of Textile Chemists and Colorists

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CALENDAR OF COMING EVENTS

Annual Meeting, Greensboro, S. C., Dec. 2 and 3.

* * *

Meeting, Southeastern Section, October 15th.

* * *

Meeting, New York Section, Oct. 28.

NOMINATIONS FOR OFFICERS

American Association of Textile Chemists and Colorists for 1933

President:—(*) P. J. Wood,
Vice-President & General Manager,
Oriental Silk Printing Co.,
Paterson, N. J.

Vice Presidents:—Two to be elected.

(*) Wm. H. Cady,
Chief Chemist,
The U. S. Finishing Co.,
Providence, R. I.

(*) Alex. Morrison,
Asst. Chemist,
American Woolen Co.,
Andover, Mass.

Treasurer:—Wm. R. Moorhouse,
Resident Manager,
National Aniline & Chemical Co.,
Boston, Mass.

Secretary:—(*) A. Newton Graves,
Chemist & Purchasing Agent,
Franklin Process Co.,
Providence, R. I.

Councillors for Three Years: Two to be elected.

Wm. D. Appel,
Chief, Textile Section,
Bureau of Standards,
Washington, D. C.

(*) Hugh Christison,
Chemist,
Arlington Mills,
Lawrence, Mass.

Councillor for Two Years: One to be elected.

Carl Z. Draves,
Chief Chemist,
Ludlow Mfg. Assoc.,
Ludlow, Mass.

(*) For re-election.

The sudden death of Mr. Harry R. Davies, Treasurer of the Association, on September 28th, necessitated a change in the nominations as originally planned. As Mr. Moorhouse, the new nominee for Treasurer, is already a member of the Council with two years still to serve, it has been found necessary to nominate a councillor to succeed him.

(Continued on page (279) 605)

Proceedings of the American Association of Textile Chemists and Colorists

The Isoelectric Point of Silk

By **MILTON HARRIS**

Research Associate of the American Associate of Textile Chemists and Colorists

Suspensions of silk in buffer solutions of different pH were prepared by grinding the dry silk fibroin to a fine powder and shaking it in the buffer solution.

Colloidal solutions of silk were prepared by dissolving the silk fibroin in a 50 per cent solution of lithium bromide and dialyzing it to remove the salt. To the solutions were added known buffer mixtures and a small amount of purified quartz powder.

Electrophoretic measurements of the suspensions of silk and of the dissolved silk adsorbed on the quartz particles gave an isoelectric point at pH 2.5.

I. Introduction

A COLLOIDAL (or other) particle is said to be at its isoelectric point when the particle is electrically neutral with respect to its surrounding medium. This point is usually defined in terms of some property such as the pH of the medium. For an amphoteric substance the acidic and basic ionization are equal at this point.

The most direct method of determining the isoelectric point is to define the conditions under which the particles do not move in an electric field. Such movement is called electrophoresis.

Electrical mobility measurements have been used in the determination of the isoelectric point of wool[1]. It is the purpose of this paper to present similar measurements of silk.

Satisfactory suspensions of wool could only be prepared mechanically, that is, by grinding the wool to a fine powder, whereas silk may be readily prepared in suspensions and in colloidal solution[2]. Abramson[3] has shown that when quartz particles are suspended in dilute protein solutions, the protein is adsorbed on the surface of the quartz particles, and the latter assumes the electrokinetic properties of the protein. This suggested a method for determining the isoelectric point of the dissolved silk.

II. Procedure

The electrophoresis apparatus and methods used in this work were the same as used in the determination of the isoelectric point of wool[1]. The silk was purified as follows: A sample of raw China silk was boiled successively in three one-half per cent solutions of soap for twenty minutes each. It was then washed with distilled water, dilute ammonia, dilute hydrochloric acid, and finally repeatedly with distilled water, at 60° C. It was then air dried for 24 hours.

One portion of the purified silk was ground in a Wiley mill. The size of the silk particles varied from 5μ to 30μ. A small amount of the ground silk was shaken vigorously with distilled water and the larger particles allowed to settle. The upper portion was carefully decanted and used for one set of measurements.

A second portion of approximately 5 grams of the silk was dissolved in 20 ml of a 50 per cent solution of lithium bromide at about 80° C. The solution was dilute to 200 ml, treated with a few drops of toluene to prevent bacterial action and dialyzed in a cellophane bag against distilled water until it gave no test for LiBr. Approximately 20 ml of the resultant solution of silk was diluted to 200 ml and the purified quartz particles described below were added. The silk-coated quartz thus obtained was used for the second set of measurements.

Quartz particles (size range 5μ to 20μ) were purified as described by Abramson[3]. Crude quartz powder was heated with a cleaning solution consisting of concentrated sulphuric acid saturated with sodium dichromate and diluted with water, for about 30 minutes. The particles were allowed to settle and the excess acid carefully decanted. A large amount of distilled water was added and the quartz suspension was filtered. The powder was washed with distilled water and then boiled with an excess of normal hydrochloric acid and allowed to settle. It was again filtered and washed with water for 48 hours.

In making the suspension to be studied, a very small amount of the quartz powder was added to the silk solution, which made it faintly cloudy.

Portions of each of these suspensions were mixed with equal volumes of the following buffer mixtures[4] with double the usual concentrations: pH 1.4 to 2.2, potassium chloride-hydrochloric acid mixture; pH 2.4 to 3.8, acid potassium phthalate-hydrochloric acid mixture; pH 4.0 to 6.0, acid potassium phthalate-sodium hydroxide mixtures.

III. Discussion of Results

The mobilities of the particles recorded in Table I are the averages calculated from ten observations.

These data are shown in graphical form in Figure 1.

[1] M. Harris, "The Isoelectric Point of Wool," Bur. of Standards Jour. of Research *8*, 779-786 (1932).

[2] M. Harris and T. B. Johnson, "Study of Silk Fibroin in the Dispersed State," Ind. & Eng. Chem. *22*, 965 (1930).

[3] H. A. Abramson, "The Adsorption of Serum Proteins by Quartz and Paraffin Oil," Jour. of Gen. Physiol. *13*, 169-77 (1929).

[4] M. Clark, "The Determination of Hydrogen Ions," 106-107. Williams & Wilkins Company.

TABLE I

Electrophoretic Mobility of Silk (Relative Velocity)		
pH	*Ground Silk*	*Dissolved Silk + Quartz*
1.42	+1.20	+1.14
1.84	+0.73	+0.79
2.13	+0.48	+0.37
2.30	+0.24	+0.26
2.54	—0.14	+0.11
2.86	—0.45	—0.36
3.00	—0.57	—0.58
3.33	—0.88	—0.82
3.69	—1.15	—1.27
4.21	—1.37	—1.40

The isoelectric point of silk obtained from the pH-mobility curve is pH 2.5. This value is in good agreement with the values obtained by Hawley and Johnson[5] and by Harris and Johnson[6] but not in agreement with those obtained by Meunier and Rey[7] and Denham and Brash[8].

Hawley and Johnson employed a U-tube electrophoresis cell and obtained values in the range from pH 1.4 to 2.8. Since the diameter of the cell was comparatively large, diffusion and convection currents made it difficult to detect small changes in protein concentration in the anode and cathode regions.

Harris and Johnson prepared solutions of silk fibroin by dissolving the degummed silk in concentrated aqueous solutions of lithium bromide and calcium thiocyanate. From solubility and viscosity measurements, values ranging from pH 2.1 to pH 2.4 were obtained.

Meunier and Rey reported an isoelectric point for silk at pH 4.2. Their results were based on the swelling of the fiber in solutions of varying hydrogen ion concentration. The curve which they obtained is flat in the region from about pH 3 to pH 6 and shows no well defined point of minimum swelling.

Denham and Brash studied the combination of acidic and basic radicals with the silk fibroin when the latter was placed in solutions of acids, bases, and salts. They, too, were unable to obtain a definite isoelectric point and concluded from their experiments that it lies between pH 3.6 and pH 4.0. However, there is ample evidence to show that the combination of proteins with positive and negative ions is not a true measure of the isoelectric point. The isoelectric point is a point of minimum and

[5]T. G. Hawley and T. B. Johnson, "The Isoelectric Point of Silk Fibroin," Ind. & Eng. Chem. *22*, 297-299 (1930).
[6]M. Harris and T. B. Johnson, "Study of the Fibroin from Silk in the Isoelectric Region," Ind. & Eng. Chem. *22* 539-542 (1930).
[7]L. Meunier and G. Rey, "Determination du point isolectrique de la laine et de la soie," Compt Rend *184*, 285 (1927).
[8]W. Denham and W. Brash, "The Isoelectric Point of Silk Fibroin," Jour. of Text. Inst. *18*, T520-5 (1927).

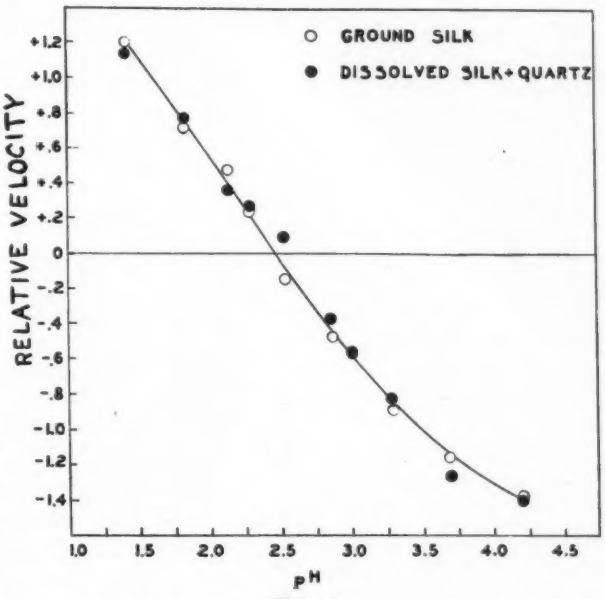

Figure 1

not zero ionization. Consequently the protein will combine with both positive and negative ions within a certain region on both sides of the isoelectric point.

The low isoelectric point of silk shows it to be one of the most acid proteins known. This is in accordance with some of the properties of silk. Meunier and Rey[7] found silk to contain only 7 parts of amino nitrogen per 10,000. The pronounced affinity of silk for basic dyestuffs is further confirmation of the predominance of its acidic nature.

The shape of the pH-mobility curve is of interest, and shows that the acidic and basic properties are less pronounced than those of wool[1]. Any changes with pH which occur near the isoelectric point are only gradual. This accounts for the large isoelectric range obtained by workers who have used less sensitive methods.

IV. ACKNOWLEDGEMENT

This investigation was made possible by a grant to the American Association of Textile Chemists & Colorists by the Textile Foundation. We wish to express our appreciation for the aid given.

Nomination of Officers

(Continued from page (277) 603)

We beg to call your attention to the following excerpt from Article VIII of the Constitution:—

"Counter nominations for any office, signed by at least ten members, may be filed with the Secretary not later than November 1."

For the Nominating Committee,

A. NEWTON GRAVES,
Secretary.

STANDARD SILK SAMPLES

There have been prepared, under the direction of the Sub-Committee on Fastness of Dyed Silk, standard dyed silk fabrics to represent four classes of fastness to washing—namely, Class I, Class II, Class III and Class IV. These standards have been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1931 Year Book.

The A. A. T. C. C. is prepared to furnish sets of these washing standards for a nominal charge which will cover the cost of preparation. It will be possible to accurately grade the fastness to washing of any dyed silk fabric by comparing it with the standards after subjection to the standard washing tests approved by this Association. All inquiries concerning these Silk Washing Standards may be addressed to the Chairman of the Research Committee,

Louis A. Olney,
Lowell Textile Institute,
Lowell, Massachusetts.

AMERICAN DYESTUFF REPORTER

Devoted to the Interests of Textile Chemistry, Bleaching, Dyeing, Finishing and Printing.

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Volume XXI October 10, 1932 No. 21

A MANUFACTURER'S STORY

AN interesting story of a large textile manufacturer is related in the October issue of *Nation's Business*. It illustrates the attitude of one representative of "big business." His story follows:

"We are a large firm, respected in the trade. But we are creaking with the responsibilities that come from age and size. The overhead of a large building designed to accommodate a demand that has subsided. Hesitance over cutting out marginal lines, for fear that new designs might not go. Old employees, most of them with us more than 15 years. Loyal? To the core. Competent? Yes. But their jaws don't stick out as they used to. Chances look bigger every year. They won't argue with me and turn the light on my mistakes as they once did. I suppose I could trade them for youngsters at half the price. But I won't. We've gone this far together. We'll go the rest of the way. Besides, youngsters irritate me nowadays.

"What a sucker we would be for some smart, aggressive young fellow, who would have no pride to swallow in doing his manufacturing in a back loft no larger than he really needed; who would have no sentimental attachment for outworn models that don't sell readily; who would employ youngsters ready to take chances, and willing at the drop of a hat to have a spirited row with a lagging production manager or an overbearing sales manager. Yes, sir, one of these days such a young fellow is going to take our measure and we'll not look too big to him. Then it will be just too bad."

There is something for the big business concern to ponder over. Has the day of small businesses passed or not?

HARRY R. DAVIES

THE death of Harry R. Davies, president of the Dyestuffs Corporation of America occurred on September 28th, 1932. He was a native of Manchester, England and was educated at the Manchester Grammar School and the Municipal College of Technology in that city. Here he took the chemistry and dyeing course under Prof. E. Knecht and was Silver Medalist in Cotton Dyeing, Ordinary and Honors, in two successive years. After graduation in 1897 he entered the employ of Levenstein, Ltd., working in the dyeing laboratory, which was then under the direction of Julius Huebner. From 1900 to 1901 he was a demonstrator at the evening class in dyeing and calico printing at the Salford Technical School with J. R. Appleyard. In 1902 he came to America to assume charge of the laboratories of Thomas Leyland & Co., who had been appointed U. S. agents for Levenstein, Ltd. Upon the formation of I. Levenstein & Co. in 1905 he became chief chemist of this concern which position he held until he was appointed a director in 1915. Early in 1924 the Dyestuffs Corporation of America was formed to distribute here the products of the British Dyestuffs Corporation and to succeed to the business of I. Levenstein & Co. Mr. Davies was elected vice-president and treasurer of the new concern and eventually became its president. He was universally popular, and was held by his contemporaries to be one of the best informed men in America on questions relating to the application of dyestuffs. He was a charter member of the American Association of Textile Chemists and Colorists and at the time of his death he was its treasurer.

HARRY R. DAVIES

CORRECTION REGARDING PROFIT IN IMPORTED DYES

Editor's Note: The appended letter from the secretary of the Synthetic Organic Chemical Manufacturers' Association is self-explanatory and quite to the point. We accept without reservation the criticism of our treatment of the matter referred to. Our only defense is that the wording of the article and the inferences likely to be drawn therefrom were entirely unintentional.

October 6, 1932

Editor,
American Dyestuff Reporter.
Sir:

Your choice of title for the editorial appearing in your issue of September 26th, namely, "Profit on Imported Dyes" was a most unfortunate one as it might easily lead to the assumption that the difference between the average unit sales value of $2.10 and the sum of the average unit

invoice value and the average ad valorem duty, a total of $1.45, was profit. Nothing, of course, could be further from the facts. The bulletin from which you quote had nothing to do with profits, actual or problematical. It was merely a check on information from various sources giving a very good clew to the portion of the total sales value of the domestic dyestuff consumption for the two years in question represented by the sales of imported colors.

In order to arrive at an estimate of the profits involved therein you would have to add the specific duty of seven cents per pound, the transportation and insurance costs, plus the importer's cost of doing business with the imported products. All of this would have to be added to the $1.45 before deducting from the $2.10 to arrive at the profit.

It is to be assumed that the importer makes a profit on his importations but to make yourself liable for the inferences that might well be drawn from your editorial is the height of absurdity.

In the utilization of any such material that comes to your attention in the future, it would be well to get in touch with the source, especially informative matter prepared for manufacturers conversant with all the details of the business. Informative material of this sort always requires supplementary interpretation in order to mean anything to those outside the industry, just as the interpretation of a chemical analysis is the important part of it and not the bald figures contained therein.

You will appreciate that all this is intended in a helpful spirit of cooperation, particularly as your publication has too good a record to spoil by making itself absurd.

Yours very truly,

SYNTHETIC ORGANIC CHEMICAL MFRS. ASS'N,

C. A. MACE,

Secretary

NEW PATENTS

Abstracted by the Synthetic Organic Chemical Mfrs. Assn.

Dyestuffs Containing Metals and Process of Making Same. (For example, comprises coupling the diazo compound of 4-chloro-2-amino-1-phenol-6-sulphonic acid with 2-amino-5-hydroxynaphthalene-7-sulphonic acid and then adding an ammoniacal copper oxide solution; dye cotton and artificial silk fast greyish tints.) Fritz Straub and Walter Anderau, of Basel, Switzerland, assignors to the Firm Society of Chemical Industry in Basel, of Basel, Switzerland, No. 1,865,978, July 5, 1932.

Brown Azo Dyestuffs. (For cotton of great brightness, good fastness to light and washing, and of good exhausting qualities, being the urea-type tetrakisazo dyestuffs.) Daniel Zinner, of So. Milwaukee, Wis., assignor, by mesne assignments to E. I. duPont de Nemours & Co., No. 1,866.786, July 12, 1932.

Brown Azo Dyestuffs. (A continuation in part of above patent No. 1,866,786.) Daniel Zinner, of So. Milwaukee, Wis., assignor to E. I. du Pont de Nemours & Co., of Wilmington, Del., No. 1,866,787, July 12, 1932.

New General Dye

The General Dyestuff Corporation has released a circular on Indanthren Brilliant Orange GR Suprafix, a new homogeneous vat color which is said to be of excellent printing properties, showing a shade, the brilliancy of which has so far not been obtained and which, it is said, cannot be imitated with any combination of other existing vat printing colors. Aside from its excellent fixation, the color is also said to produce shades of superior fastness to light, boiling, and washing and chlorine.

S.O.C.M.A. Meeting

The first fall luncheon and general meeting of the Association was held at the Princeton Club, New York City, on Thursday, September 15th.

President Merz introduced to the members present Mr. Dexter North, chief of the Chemical Division of the U. S. Tariff Commission, and his assistant, Mr. P. K. Lawrence. Mr. North spoke briefly about his recently issued request for production and sales reports of synthetic organic chemicals, coal-tar and non-coal-tar, for the year 1931, explaining that this was in no sense to be considered as a continuation of the detailed Census but a part of the duty of the Tariff Commission under Section 332 of the 1930 Tariff Act.

The meeting adjourned at 2:15 P. M.

Opens Additional Plant

Announcement has been received that Jacques Wolf & Company has added another unit by the purchase of additional property and building at Carlstadt, N. J. This new plant was purchased by Jacques Wolf & Company to enable them to extend their manufacturing facilities.

It has also been learned that at a recent meeting of the board of directors of that company, Gerald J. Desmond, who has become well known in the textile trade through his energetic efforts as sales manager, was elected a director and secretary of the company. In his new capacity, Mr. Desmond will continue his personal contact with the dyers and printers in the vicinity of Paterson and other textile centers of the East and South.

Pontacyl Fast Brown CGS

The dyestuffs division of E. I. du Pont de Nemours & Company announces the development of Pontacyl Fast Brown CGS, a homogeneous acid dyestuff giving rich, reddish brown shades on wool and silk. The product is used mainly as a self-color brown but it is expected it will be of value in small quantities for shading other acid colors possessing the same properties. It is fast to fulling for an acid color and exhibits excellent general fastness to all destructive agents except light. The light fastness of Pontacyl Fast Brown CGS is, however, sufficiently good for all ordinary silk and wool requirements.

The New Rigid Tube Package Dyeing Machine

After studying for many months the merits and faults of the rigid tube package dyeing system, the Franklin Process Company has decided to market a machine of this type as an addition to its regular line of Franklin Process Package Dyeing Machines.

This new machine, however, departs from the conventional design of most other machines of this type, and offers the following features: Low loading and unloading time, short dye bath, little floor space, low cost of upkeep, low labor cost, and a one-unit system, which assures maximum production under average dyehouse conditions.

BEFORE explaining the advantage of this machine in detail, and in order to thoroughly appreciate the significance of this latest offering to the yarn dyeing industry, it is necessary to review the history of package yarn dyeing machines.

History

The first package yarn dyeing machines were invented in Europe, probably over 40 years ago. All of these European machines seem to have had one thing in common; namely, the packages or cheeses were wound on rigid perforated tubes. (Fig. 2.)

These first European machines had a very limited sale in the United States, but were never widely accepted because of trouble with uneven dyeing. Much of this trouble seemed to be due to the fact that some packages were harder than others, received less dye liquor and, consequently, were dyed lighter in shade than others or were not penetrated at all in spots.

Presumably, if all the packages had been wound with the same density in all parts at all times, this difficulty would not have been experienced. However, such a condition seldom pertains in actual manufacturing. The problems, therefore, was to devise some means of equalizing the density of all packages *in the dyeing machine*.

The problem was solved by the Franklin Spring Tube (Figs. 3 and 4) which consisted of a spiral spring either 3 inches or 6 inches long, and a knit cover or sleeve. This spring tube was invented by Mr. Daniels of Franklin, New Hampshire, and was first offered to the trade in 1910.

European Type Machines Reappear in American Market

About six years ago, after more than 20 years virtual absence, the European type package dyeing machines again appeared in the American market. Having been so long absent from the United States, the impression has been, since their reappearance, that they are something new in principle. Such is not the case, however, since these machines still employ the rigid tube as did the European machines of 40 years ago. No doubt, they represent many minor improvements over their predecessors, but in principle they remain unchanged.

These rigid tube machines, however, now face a different situation in the United States than they did 20 years ago. During this interval the American textile industry has become thoroughly educated on the advantages of package dyeing. The *method* no longer has to be sold in most cases. The *brand* of package dyeing machine is now the only matter open to question. Consequently, these European type machines have received a much more cordial reception this time than they did at the time of their first appearance.

The Advantage of the Rigid Tube

The advantage of the standard 5/8" diameter rigid paper or composition tube (perforated) is that it enables the spinning mill to wind yarn directly to the dyeing package from the spinning or twister bobbin, instead of to the ordinary solid paper tube or cone. In this way an extra winding operation is eliminated before dyeing.

As a matter of fact, some spinning mills can wind Franklin packages in the same way. However, these mills have to equip their winding machines with special arbors in order to accommodate the spring tube, which is 1 5/8" in diameter. This, of course, involves a certain amount of expense and many spinning mills have hesitated to equip to wind packages for this reason.

Some mills have also objected to furnishing packages because when they do so they have to borrow the spring tubes from the mill buying the yarn. While this does not involve any important expense, it does constitute an annoyance to some mills and necessitates keeping track of the springs on memo, which is somewhat of a bother.

Perforated tubes, on the other hand, are purchased outright like standard paper tubes, and after being once used, are thrown away. In other words, they involve no paper work.

Disadvantages

To offset this fact, perforated tubes cost considerably more than ordinary paper tubes and thus add to the expense of the spinner. In the past, spinning mills have been able to get an extra cent per pound of yarn to take care of this cost, but competition seems to have effectively eliminated this charge at present, so that the advantage is now all with the purchaser of the yarn.

Mill That Spins Does Not Benefit

The foregoing is of interest to the mill that buys its yarn. On the other hand, it is of no significance to the mill that does its own spinning. Such mills can wind direct from spinning or twister bobbins to spring tubes just as the spinning mill winds direct to perforated tubes, and the spring tubes do not have to be shipped out because the yarn is used in the mill.

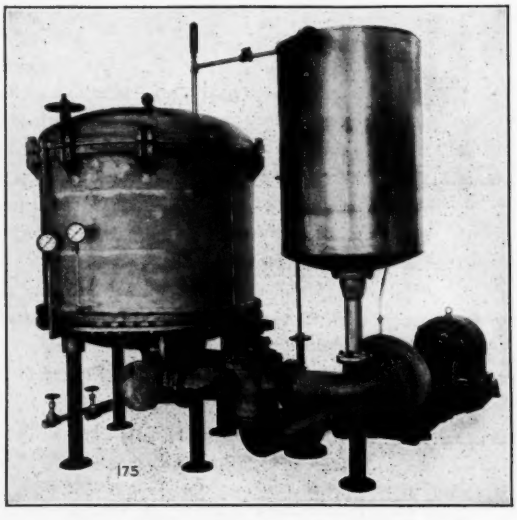

Fig. 1
Franklin Process Package Dyeing Machine. The outside appearance of the spring tube machine and the rigid tube machine is approximately the same.

To be sure, in this case there is the expense of special arbors for the winding machines and of the springs, but this expense is balanced by the fact that it is a one-time expense, whereas new perforated paper tubes have to be purchased continually.

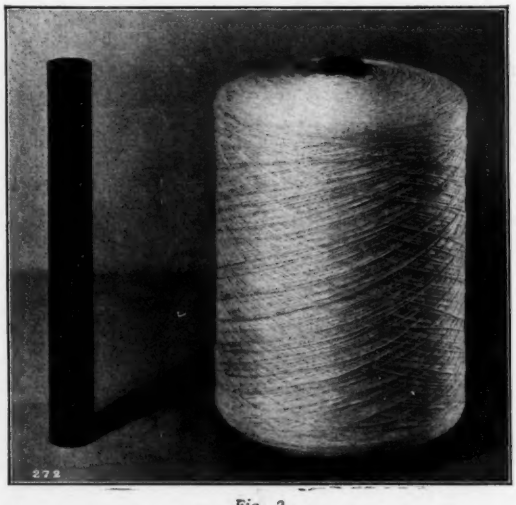

Fig. 2
A 5/8" diameter rigid perforated tube and a European type of dyeing package or cheeses wound on such a tube.

In some cases where the class of work demands it, European type machines use perforated metal tubes instead of perforated paper tubes. These can be used over and over again like the spring, but they have no advantage over the spring because they cost even more.

There are also the knit covers or sleeves, which form a part of the tubes, to be considered. While these can be used several times in many cases, they do represent a continuing expense. This is more than balanced, however, by the considerably greater continuing expense of the perforated paper tubes. Furthermore, knit covers frequently have to be used with perforated paper tubes as well as with springs, in order to prevent white cross-overs on the yarn down next to the tube.

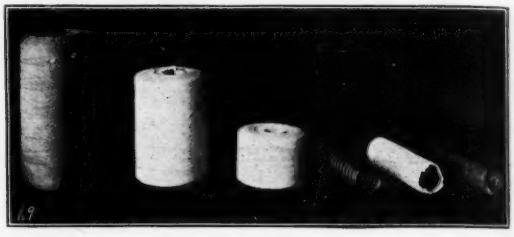

Fig. 3
9", 6" and 3" Franklin Packages or cheeses. Also Franklin Spring, Franklin Tube (consisting of spring and knit cover) and wooden core for spring when rotating package in a creel. The spring permits packages to be compressed in the dyeing machine, so that harder and softer packages are equalized in density and thus dyed the same depth of shade.

All things considered then, it appears that rigid tube dyeing machines offer special advantages chiefly to the mill that does not spin yarn. For such a mill they eliminate an extra wind which might be necessary if the yarn were purchased from a mill that was not equipped to wind on springs.

Fig. 4
Showing Franklin Packages before and after being compressed on machine spindles.

European Machines More Favorably Received

Because of this advantage, rigid tube package dyeing machines have made much more progress in recent years than they did during their previous assault on the American market 20 or more years ago. Nevertheless, it is true that while the rigid perforated paper tube gains advantages in one respect, it loses advantages in other respects. For instance:

Weaknesses

These tubes at times collapse in the dyeing machine due to extra long dyeing time, high temperature and

chemicals used. For this reason, it is sometimes necessary to substitute the rigid metal tubes. This immediately nullifies the advantage offered by the paper tubes. In other words, the metal tubes are just as expensive as, or more expensive than, springs. Therefore, they have to be loaned to the spinner and shipped back and forth just like springs.

In cases where perforated paper tubes are used, they still have a tendency to collapse in the extracting even though they do not collapse in dyeing. To overcome this, it is necessary to insert wooden plugs in the tubes before extracting and to remove them afterward. This extra labor, of course, involves extra cost.

In order to eliminate the need of inserting these wooden plugs, small extractors have been put on the market that handle one package at a time. The packages are put over a center spindle which holds the tube in shape. While these extractors have proved efficient as regards the removal of water, it has yet to be demonstrated that they spring tube. This is necessary because the effect of extra hard packages cannot be neutralized to the same extent in a rigid tube dyeing machine as in a spring tube machine. While this soft winding improves the dyeing properties of the package as regards rigid tube dyeing, at the same time it seriously impairs its unwinding qualities, either for rotation or overend delivery.

When rotating a soft package, the end has a tendency to bury itself, causing undue strain and breakage. When delivering overend about one-half or two-thirds way through the package, the yarn fails to balloon properly. The extra drag thus developed causes excessive breakage. This trouble is aggravated by the small diameter of the tube (5/8") as compared with the diameter of a Franklin tube which is 1 5/8". In other words, the smaller the diameter, the less the whip.

The defects so far mentioned, it will be noticed have been related to the package, and not to the machine or to the dyeing results obtained.

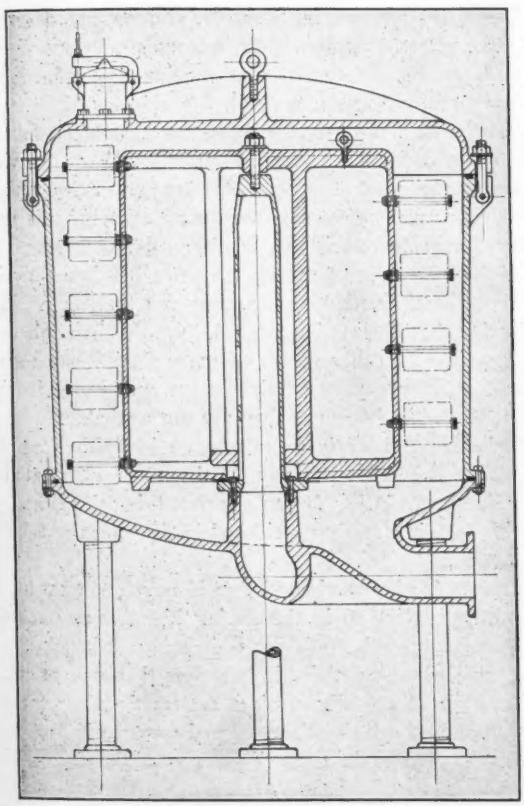

Fig. 5
Cross section of European type rigid tube package dyeing machine. Note excessive amount of dead space (not filled with yarn) as compared with a Franklin Process Machine. This means a longer dye bath and more floor space per pound of yarn dyed. Also note that packages unequal in density must remain so during the dyeing operation, since they are on rigid tubes and cannot be pressed together.

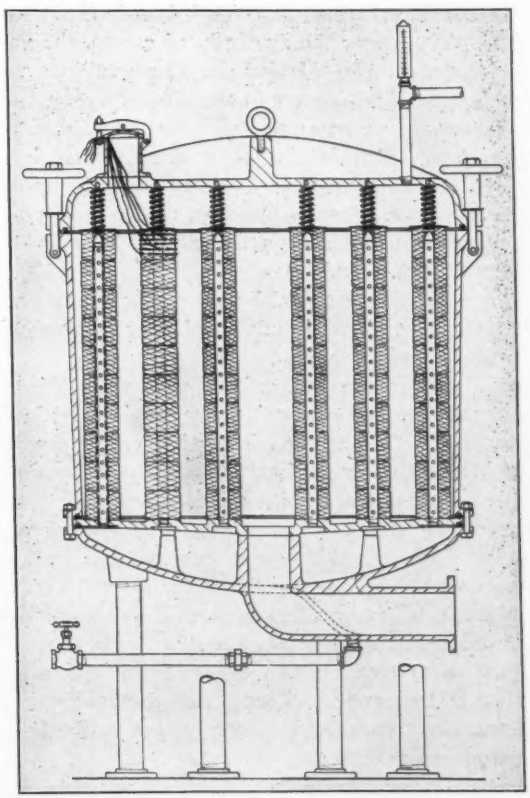

Fig. 6
Cross section view of Franklin Process package yarn dyeing machine, showing how packages or cheeses are compressed on the perforated spindles, so that all packages have an equal density. Thus, these packages all receive an equal amount of dye liquor and are all dyed the same depth of shade. Also, note small amount of dead space as compared with European type of machine.

can handle a large production at a cost comparable with that of an ordinary whizzer that holds several hundred packages.

It is also true that a package to be dyed in a rigid tube must be wound softer than a package to be dyed on a

The average European type of package or cheese dyeing machine uses more horse power than a Franklin Process type of machine of equal capacity. For instance, one make of this type uses a 50 H.P. motor for a machine with a capacity of 464 packages, whereas a Franklin

Process Machine with a capacity of 480 packages uses a 15 H.P. motor. This excessive horse power is, no doubt, used in an attempt to overcome inequalities in densities of packages by sheer force of pressure. It is also probably due to the fact that the average European type of cheese or package has a thicker wall than does the Franklin package. For instance, 1-11/16" compared with 1-7/16".

In this connection, it is important to note that although the average European type of package has a thicker wall than does the Franklin package, it does not contain as much yarn. The average European type of package contains about 16 oz. of yarn, whereas the average 6-inch Franklin package contains about 20 oz. of yarn. This decrease in yardage, of course, makes more frequent doffing necessary and, hence, increases winding costs.

All European type machines that have come to the author's attention also have a longer dye bath than that of the Franklin Process Machine, the ratio apparently being at least 12 pounds of liquor to 1 pound of yarn. In the Franklin Process Machine it is only about 8 to 1, or less. The longer the dye bath, of course, the greater the cost of dyestuffs, chemicals, and steam.

The explanation seems to be that the longer dye bath in the European type of machine is unavoidable due to the construction. That is, the center drum, or carrier, requires a certain amount of dead space which cannot be filled with yarn, whereas the Franklin Process type of kier permits a much larger proportion of the space to be utilized. (Figs. 5 and 6.)

This dead space required by the center drum, or carrier, also reflects itself in additional floor space required for a given production.

Perhaps one of the most serious faults of the European type of machine is the excessive time required for loading and unloading. To be sure, it requires only a few minutes to lower the carirer into the machine or to remove it, but this represents only a minor part of the loading and unloading time. The greater part of the loading and unloading time with this type of equipment is consumed in fastening and unfastening the packages on the holders. For instance, with regard to one particular make of European machine, it has been reported that for a production of 8,000 pounds a week, two men full time are required to screw and unscrew packages from the holders. The significance of this defect is better grasped by the following comparison:

LOADING AND UNLOADING TIME

European Type Machine with Drum Carrier

(*Capacity*—232 *Packages*)

	Minutes
Fastening 232 packages on spindles	45
Raising and lowering drum into place	5
Removing drum from kier after processing	5
Unfastening 232 packages from spindles	45
Total loading and unloading	100

Franklin Process Type of Machine

(*Capacity*—288 *Packages*)

	Minutes
Dropping packages on spindles	15
Removing packages from spindles	7
Total loading and unloading	22

A THREE-UNIT SYSTEM

The European type machines which have made the greatest progress in this country have been on the three-unit system; that is, one unit for boiling-out, one for dyeing, and one for finishing. The idea, of course, is patterned after the specialized machine methods used in automobile factories and similar places, and the equipment as laid out is quite impressive. Because of the associations, the prospective purchaser is apt to assume immediately that the production by this method is greater and cheaper than with a single-unit, multi-purpose system where boiling-out, dyeing and finishing are all done in one kier.

The three-kier system, however, will not stand careful analysis. In the first place, it assumes continuous production but, as a matter of fact, continuous production in the average dyehouse is a myth.

Another weakness of the three-kier system is that the production of all three units is limited by that unit which consumes the greatest amount of time per batch—namely, the dyeing unit. The maximum production of this unit, under favorable conditions, would probably average not more than 8 batches per day, allowing 1¼ hours dyeing time per batch, and no extra time for matching. It is futile for the other units to produce more than this even if they can. In other words, if more than 8 batches are boiled out they cannot be dyed anyway. More batches cannot be finished because they are not available.

To be sure, there is an advantage in boiling-out one more than 8 batches per day, in that one extra batch is immediately ready for dyeing the first thing the next day, but this fact is already considered in figuring the 8-batch production.

It must also be considered that if any batch has to be redyed, or is delayed in the dyeing kier for any reason, the production of the finishing unit is also delayed.

In actual practice, then, it is a fact that one or more units of the three-kier dyeing system is always non-productive part of the time. Furthermore, if the production is divided between light and dark shades, the dyeing unit must be boiled out before a light shade can follow a dark shade. This means more delay for the other units and makes the theoretical production impossible.

A fair comparison of the three-unit and one-unit systems of package dyeing can be made only on the basis of the same number of units for both, because only on this basis are the investments required at all comparable. Comparisons are not always made on this basis, which leads to an erroneous impression in favor of the three-unit system.

The following chart, it is believed, gives approximately the correct picture:

3-Unit Package Dyeing System		1-Unit Package Dyeing System
Capacity per unit— 464 *packages*		*Capacity per unit—* 488 *packages*
Operation	*Time*	*Time* — *Operation*
Boil-out		Boil-out, dye and finish
Dye	1¼ hrs. for one batch	3-1/3 hrs. per 3 batches — Boil-out, dye and finish
Finish		Boil-out, dye and finish
10-hour day divided by 1¼ hrs. per batch equals 8 batches per day.		Each machine will do 3 batches per day, making a total of 9 batches.
Total production — 3,712 packages.		Total production — 4,392 packages.

Investment is approximately the same in both cases. If there is any difference, it is in favor of the one-unit system.

Labor Cost

It has already been shown that more labor is required to load and unload the European type of package dyeing machine than to load and unload the Franklin Process type of machine. In addition, it should be remembered that for a given production the three-unit system requires more machines than does the Franklin Process. Therefore, as the labor required for one machine, is distributed over less poundage, the labor cost must be greater. It has been estimated that the labor cost for the European system is at least one-half cent more per pound than for the Franklin Process.

Breakage of Spindles

The spindles which project from the carrier of the European type machine, and on which the packages are placed, also present a problem. Projecting from the sides of the carrier, they are exposed to severe strains as the carrier is knocked against the side of the machine, the columns in the dyehouse or the wall. As a result, frequent breakage is the rule and excessive maintenance cost in this one respect naturally follows. Vibration is an even more serious cause of breakage of this type.

Rigid Tube Dyeing Machines Have a Following

In spite of these failings, the European type of package dyeing machine has its followers. The chief reason for this, perhaps, is that the idea of being able to buy yarn in the open market all wound on perforated tubes for dyeing has taken a strong hold upon the imagination of the textile industry.

Such being the case, the Franklin Process Company stands ready to give the textile industry what it wants. At the same time it still retains the Franklin Process spring tube dyeing machines in its line and still believes that this type of machine produces the best in quality and has the widest application.

Furthermore, the company, in taking this step, does not propose to follow blindly in the footsteps of its predecessors in the rigid tube package dyeing field. It has sought to retain in its new machine all the advantages of the European type and, at the same time, to eliminate the serious disadvantages. In addition, it has also included the advantages of the older type Franklin Process machine, with the exception of the spring tube.

The result is as follows:

Minimum Loading and Unloading Time

To overcome the excessive loading and unloading time required by the European type of package dyeing machine, the Franklin Process rigid tube dyeing machine does not use the removable drum carrier with a separate spindle for each package. Instead, the method of loading and unloading is just the same as with the older type of Franklin Process machine. That is, the holders, or carriers, are vertical spindles of special design permanently attached to the bottom of the machine. When loading, four or five packages are dropped on each spindle. There are no caps to be screwed on or fasteners of any kind. The packages are automatically held in place by means of a patented spring and plate device on the bottom of the cover. The plates rest on the top package of each spindle column when the cover is lowered into place. After dyeing, the packages are unloaded by hand with the aid of a specially designed forceps.

Shortest Dye Bath

The elimination of the drum carrier in the Franklin Process rigid tube dyeing machine automatically eliminates the longer dye bath used by the European type of machine. The length of the dye bath in the Franklin Process rigid tube machine is just the same as in the Franklin Process spring tube dyeing machine—namely, 8 pounds, or 1 gallon, of liquor to 1 pound of yarn.

Minimum Floor Space

This advantage of the older Franklin Process spring tube dyeing machine has been retained in the newer, rigid tube dyeing machine, due to the fact, of course, that there is no drum carrier to create dead space.

No Breakage of Spindles

The frequent breakage of spindles encountered with the European porcupine, drum type of carrier is eliminated in the Franklin Process rigid type dyeing machine.

It will be recalled that the holders in this machine are not lifted out with the yarn. They consist merely of specially designed vertical rods permanently attached to the bottom of the machine, the tubes, themselves, forming a circulating pipe. These rods are not exposed to rough treatment and their life is indefinite.

Lowest Labor Cost

The elimination of extra labor for loading and unloading carriers and the fact that more yarn is confined in a given space, naturally reduce the total labor cost for the Franklin Process rigid tube dyeing machine. In fact, the labor cost of this machine is just the same as for the older type of Franklin Process machine. While costs vary in different plants, as already stated, comparable situations indicate that the labor cost with a Franklin Process type of machine is about one-half cent lower than with the European type of package dyeing machine.

One-Unit System

Like the Franklin Process spring tube dyeing machine, the Franklin Process rigid tube dyeing machine is offered in the one-unit system only, because it has been demonstrated that with a given investment, this system gives greater production at lower cost.

Standard 5/8" Diameter Tube

The advantages of the Franklin Process rigid tube dyeing machine which have just been mentioned are not found in the European rigid tube dyeing machines commonly used in the United States. In addition, of course, the Franklin Process machine has the advantage common to nearly all rigid tube machines—namely, the use of a standard 5/8" diameter perforated paper tube, which makes it possible to purchase for this machine natural cotton yarns all wound for dyeing at regular competitive prices.

The disadvantages which are inherent in rigid tube dyeing cannot, of course, be eliminated in this new type of Franklin Process machine. The disadvantages referred to are softer packages that do not deliver so well as the spring tube package, and the absence in the dyeing machine of any means of compensating for variation in density of packages.

In some cases, it is appreciated that these disadvantages may not be serious and that in other cases extra careful supervision will minimize them. For such situations, the Franklin Process rigid tube dyeing machine is offered with every confidence of its efficiency as compared with other types of rigid tube machines.

For the best quality, however, and for the greatest adaptability, it is claimed that the Franklin Process spring tube type of machine is still superior.

White Discharges on Silk with Hydrosulphite

(Continued from page 600)

The only thing to do is to throw the paste away and make another start.

In the case of thickeners that are cooked in the color shop, the best way to incorporate the Hydrosulphite is to cook the paste as usual, shut off the steam, and add the solid material. Allow to run for about 15 minutes to insure complete solution, and then turn on the cold water and cool the thickener.

When using Gum Arabic the gum is cooked in the usual manner, taken out of the kettle and allowed to settle in a barrel to get rid of the grit. Then 30 gallons of this gum are placed in a kettle, heated to a temperature of 160-180° F., and 200 pounds of Hydrosulphite are put in and stirring continued until solution is effected. The kettle is then filled up with gum to the 50 gallon mark. Textile Gum may be taken direct from the barrel in which it is received and heated and handled just like Gum Arabic.

If the thickeners are prepared with a Hydrosulphite content of 4 pounds to the gallon there is plenty of leeway in adding the other necessary ingredients when making up the white discharge for the printing machine. A gum too weak in Hydrosulphite cripples the color shop to some extent should the batch come out on the thin side, as does at times happen even under the most careful supervision.

The Ageing and Washing of White Discharges

It is impossible to give exact detailed instructions for the ageing of white discharges that will suit every mill, since local conditions show so much variation. However it can be said that the ager should not be too dry, nor the temperature too high, otherwise imperfect discharges will result, and even a second or a third ageing will not give satisfactory results. On the other hand, extreme dampness in the ager means a danger of marking off, and in the case of weighted silks it will also cause the formation of brownish stains in the printed parts, due to the production of Sulphite of Tin. These stains may also be produced by giving the goods too long a time in the ager.

When this brown stain appears it may, except in extreme cases, be removed in the washing. One method is to wash in a very weak Caustic solution in the dyebeck. If this is done great care should be taken to see that the alkali is thoroughly neutralized in the subsequent washings. Perhaps a better method is to pass the goods through a weak solution of Hydrogen Peroxide at a temperature of 140° F. on the open washer. Whichever method is used a subsequent washing with soap as hot as the ground shade will stand, will effect an improvement.

A METHOD FOR DISTINGUISHING BETWEEN OLD AND NEW COTTON FIBRES

(Continued from Page 602)

the above causes the stain is taken up more intensely by the inner cellulose structure of the fiber than by the cuticle. The cuticle stains an even pink color, while the inner material assumes a deep red color on contact with the dye. If the outer cuticle is not damaged in any way, it is not broken and the dye cannot reach the inner cellulose and we observe a uniform pink color on the fibers

Methylene Blue Test

The method is said to be capable of detecting any of the above mentioned kinds of damages to the slightest degree. Our experiments along this line were carried out on known samples of bedding materials and indicated that the degree of damage by ageing or use in bedding or furniture is insufficient to make the Congo Red test conclusive, if used alone.

Several samples of old and new bedding materials were subjected to the Methylene Blue test. The purpose of the test is to detect the presence of oxycellulose in cotton cellulose. Since oxycellulose dyes a deeper shade of blue than cellulose, it may be easily detected. Oxycellulose was found to be present in all of the samples but no accurate correlation of the age of cotton fibers with the amount of oxycellulose present was obtained. The old samples were found to contain appreciably more oxycellulose than the corresponding new samples. However, it was found that samples of new low-grade linters gave a much deeper Methylene Blue reaction than did samples of old cotton of a better grade. Consequently, an analyst cannot positively identify the age of a sample of cotton using the Methylene Blue test alone. Another re-agent, Prussian Blue, was subsequently used in place of Methylene Blue. This proved to be more effective than the former. The color was much more distinct, the oxycellulose being dyed a deep blue, while the cellulose was only slightly colored. The results of this test corresponded very well with the results of the Methylene Blue test, but this method alone is not particularly conclusive.

The Copper Number

Several investigators have concluded that the action of sunlight on cotton in the presence of air was an oxidation process somewhat similar to that caused by chlorine. The ultimate substance, oxycellulose, is capable of reducing alkaline solutions of copper sulphate and silver nitrate. The reducing power is generally expressed, in the case of copper sulphate, as the amount of copper which would be reduced by 100 grm. of cotton treated with an alkaline copper sulphate solution and is known as the Copper Number of the sample. Similarly, the silver solution reduction is expressed as the Silver Number. The reducing power of the oxycellulose was found to bear a linear relation to the length of exposure.

The findings of these investigators suggested to us the application of the Copper Number determination to our problem since it would give a quantitative method for ascertaining the amount of oxycellulose present. Our examination of corresponding samples of old and new cotton gave quite distinct differences in the amounts of oxycellulose present, but, as in the Methylene Blue tests, we found that the percentage of oxycellulose in new low-grade linters was higher than in old samples of better grades. A similar series of samples was submitted to the Silver Number determinations with results that paralleled the Copper Numbers. While the results of these tests were consistent with what was expected, we found that they afforded no certain method of ascertaining the age of the cotton samples examined if their nature was not previously known.

Conclusion

While examination of samples of material directly in the ultraviolet rays is sometimes conclusive, particularly in the case of material which is either all new or all old this method alone should not be depended upon for correct results if new and old materials are mixed as by garnetting, but tests should be conducted as outlined above, for determination of the presence of oxycellulose, and for damage to the fibers by heat, fungi or by mechanical means.

Production of Anti-Crease Fabrics*

SO FAR as we can ascertain the Tootal Broadhurst Lee Co., Ltd., has obtained three British Patents in connection with creaseless fabrics. B.P. 291,473, taken out by the company and R. P. Foulds, J. T. Marsh, F. C. Wood, H. Boffey and J. Tankard, states that cotton, silk, wool, ramie, jute, hemp, artificial silk, acetyl silk or linen or mixtures of these fibers, are rendered creaseless by effecting the final condensation or polymerization of a synthetic resin in presence of the textile material. So far as wool is concerned, the process only relates to the lower grades, the best qualities being naturally uncreasable to a large extent.

The method of preparation of the intermediate resin must be chosen according to the nature of the material to be treated. Some solutions containing free phenol, for instance, would dissolve acetate silk, while other solutions would destroy hemp or jute and so on.

The patent points out that it had already been proposed to incorporate a synthetic resin and a filler in fabrics with the object of making the filler more permanent, but the procedure differed essentially from the conditions necessary for the production of uncreasable fabrics. It had also been proposed to use synthetic resins for stiffening and for forming composite materials. None of these earlier processes aimed at producing uncreasable goods, nor would the directions given yield such fabrics.

*Dyer.

The patent contains examples of the application of the process in which urea is used, a urea-formaldehyde resin being formed. The fabrics retain their suppleness and the conditions employed are such that the fibers are not tendered.

A subsequent patent—291,474—deals solely with cellulose fibers and the production of the non-crush effect by means of a condensation product of a phenol and a formaldehyde.

The third patent is B.P. 304,900. According to the process it protects, a particularly advantageous method of obtaining a non-crush cellulosic fabric, with special reference to the object of retaining as far as possible its original strength, is to impregnate the fabric with a synthetic resin or its components while it is in the wet state, final condensation being effected so as to produce a fabric which will not crease. In a preferred form of the process, the fabric is first thoroughly treated with caustic soda, the cellulose thereby becoming considerably swollen. The caustic soda is removed by washing and the fabric then squeezed until it contains 100 per cent or more of water. In its wet state the fabric is run into a reaction mixture consisting of 100 parts of weight of phenol, 100 parts of 40 per cent formaldehyde, 4 parts of potassium carbonate, which have been boiled together for five minutes and rapidly cooled.

After impregnation with the reaction mixture in a mangle the fabric is squeezed so as to retain about the same weight of liquor as formerly and dried at a low temperature or the temperature of the stenter. It is finally heated for two minutes on drying tins at 170 deg. C., so as to insolublize the resin and produce the desired property. A soaping process is then applied to remove excess reagents, and after washing and drying the treatment is complete.

Opens Fall Session

The North Carolina State College Textile School opened its fall session on September 23rd with bright prospects for a successful year. The faculty, which has served the Textile School efficiently, has been kept intact and the present registration exceeds the undergraduate enrollment of the past two years. It is expected that there will be an increased enrollment during the first term.

DYER—A-1 dyer of cotton and rayon piece goods mixtures in all styles and weights seeks position. Has made a specialty of fast colors, including vats, indigosols, developed work for discharge printing, sulphurs, direct and basics. Vats reduced continuous or pigment process to pass Nafel test. Other work on pads, jigs, continuous machines or reels. No experimenting—accurate matches right away. Technical Institute graduate in chemistry and dyeing. Address replies to Box No. 754, American Dyestuff Reporter, 440 4th Avenue, New York City.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

CLASSIFIED

EXPERIENCED SALESMAN - DEMONSTRATOR, Chicago Territory. Has thorough knowledge of all dyestuffs, imported as well as domestic, their application, and the use of all finishing materials, water softeners, penetrators, etc. Practical Dyehouse experience. References. Address Box No. 740, American Dyestuff Reporter, 440 Fourth Avenue, New York.

DYESTUFF SALESMAN—With fifteen years' experience, chiefly in Empire State and New Jersey is at liberty and desirous of position with manufacturing concern. Address Box No. 748, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

BLEACHER, Assistant Dyer (cotton and wool) and Textile Chemist, desires position. Experience in water treatment and development work. Location immaterial. References. Address Box No. 751, American Dyestuff Reporter, 440 Fourth Avenue, New York.

WANTED—For New Jersey concern, *color dyer on skein silk*. Very exact matching required. State age and previous experience. All communications strictly confidential. Address Box No. 752, American Dyestuff Reporter, 440 Fourth Avenue, New York.

TEXTILE SALES EXECUTIVE with technical education and practical experience in knitting weaving and dyeing, last five years in Middle Atlantic States and previously in the South, especially qualified for selling synthetic yarns, silk throwing, dyestuffs and dyeing machinery. Will be interested as direct representative or manufacturer's agent. Address, D-8, 437 West School Lane, Philadelphia, Pa.

SALESMAN—wanted by large dyestuff manufacturer for Southern New England territory, Salesman-demonstrator about 35 years old having thorough knowledge of all dyestuffs and their application. Address Box No. 753, American Dyestuff Reporter, 440 Fourth Avenue, New York City.